

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.

THIS PAGE BLANK (USPTO)

Akt

PATENT SPECIFICATION (11) 1413651

1413651

- (21) Application No. 51307/71
- (22) Filed 4 Nov. 1971
- (23) Complete Specification filed 1 Feb. 1973
- (44) Complete Specification published 12 Nov. 1975
- (51) INT CL² B22D 23/08
- (52) Index at acceptance C7X 1



(54) IMPROVEMENTS RELATING TO THE ATOMISING OF METALS

(71) I, ALFRED RICHARD ERIC SINGER, Department of Metallurgy, University College, Singleton Park, Swansea, British, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Metals are often required in the form of unoxidised dry powders. One of the standard methods of obtaining metals in this form is by gas or air atomising and a second method is by water atomising. Gas atomising has the advantage of producing a dry powder directly, but large volumes of relatively expensive inert gas may be necessary to avoid oxidation and ensure adequate atomisation together with subsequent chilling of the liquid metal droplets to form solidified powder particles. Water atomising, on the other hand, ensures heavy chilling of the liquid droplets but yields a wet powder, frequently partially oxidised, which has subsequently to be dried before use.

The present invention enables dry unoxidised atomised metal powder or solidified particles to be produced using smaller volumes of gas, which may be less pure than hitherto, together with the injection of hydrocarbon and water; the combined fluids giving a much higher degree of chilling of the powder or particles than by normal gas atomising. The invention consists of atomising liquid metals with fluids consisting of nitrogen which may contain limited quantities of free or combined oxygen, a hydrocarbon or a mixture of hydrocarbons mainly in liquid form, and water.

The invention may be applied to the atomising of most metals including copper and iron and their alloys. It is particularly useful for iron where low cost and the formation of a powder relatively free from oxide is required. Aluminium and stainless steel may be atomised in this way but both aluminium and chromium have a great affinity for oxygen so that skins of Al_2O_3 and Cr_2O_3 will be

formed when either free or combined oxygen in the form of water or carbon dioxide is available in the system.

In subsequent descriptions the examples used and the arguments put forward are concerned with the atomisation of carbon steels. However the method and the equipment are not limited to such use and may be applied to a wide range of ferrous and non-ferrous metals and alloys.

The nitrogen used as the main gaseous atomising fluid can be of high purity or it may with economic advantage be of much lower purity, perhaps containing small quantities of free oxygen, water vapour or oxides of carbon. Whereas nitrogen of such low purity would cause appreciable oxidation of iron when using normal atomising procedures, it is wholly satisfactory and may be rendered non-oxidising when used in conjunction with hydrocarbon and water injection. A cheap form of nitrogen of adequate purity for use in conjunction with hydrocarbon injection is the cleaned flue gas resulting from the burning of hydrocarbon fuel with air. Such gas after cooling, condensing surplus water and compressing to the atomising pressure is extremely cheap and consists of N_2 , water vapour, CO and CO_2 . It is not necessary to free such gas from water vapour or the oxides of carbon, it is merely necessary to know its composition in order to ensure a correct balance of hydrocarbon and water during the atomisation process. The reactions occurring in the atomising chamber are complex and are temperature dependent. Because the atomisation process involves a rapid fall in temperature from 1600°C to say 700°C in the case of steel, the normal thermodynamic data are, unfortunately, of limited value.

The first reaction that occurs when hydrocarbon is injected into the stream of liquid iron at high temperature is that the hydrocarbon is cracked to form carbon, hydrogen and small residual amounts of lighter hydrocarbon. The finely divided carbon reacts at

50

55

60

65

70

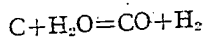
75

80

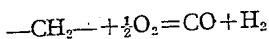
85

90

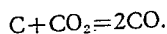
high temperature with the water vapour provided by the injected water, the iron acting as a catalyst, to produce carbon monoxide and hydrogen with the absorption of heat in accordance with the following equation:



It is important to note that the amount of free oxygen in the nitrogen should be strictly limited because such oxygen combines with and burns part of the hydrocarbon injected into the gas stream. While the products of such partial combustion promote reducing conditions in the atomising chamber as shown by the following equation:



the heat generated has the undesirable effect of reducing chilling of the liquid droplets subsequent to atomisation. The amount of combined oxygen in the form of water vapour, carbon monoxide or carbon dioxide which can be tolerated in the nitrogen is much greater than the amount of free oxygen, because the water and carbon dioxide react at high temperatures with the carbon resulting from the cracking of the hydrocarbon to form carbon monoxide and hydrogen with the absorption of heat in the case of water. Carbon monoxide is formed in the case of carbon dioxide according to the following equation, the carbon monoxide being more stable at higher temperatures:



The maximum amount of free oxygen that can be permitted depends upon the degree of chill required but more than 2% of free oxygen will cause a considerable reduction of chill.

The term hydrocarbon is used to cover compounds, or mixtures of compounds, the molecules of which consist mainly of carbon and hydrogen atoms, although atoms of some other elements such as oxygen may be present in small amounts. For most purposes relative freedom from certain deleterious elements such as sulphur and phosphorous is required to avoid contamination of the atomised metal product. Gaseous hydrocarbons such as methane or natural gas may be used effectively in the invention but the amount of chilling and the amount of heat extracted during atomising is not so great as in the case of a liquid hydrocarbon. However, such gaseous hydrocarbons have the advantage that when delivered at high pressure they can replace up to 90% of the nitrogen as the atomising gas. An appropriate injection of water is necessary to balance the hydrocarbon and increase the chilling effect.

An important feature of the process is the

need to obtain a suitable balance of the various reactants used in the atomisation in order to ensure that atomised iron or steel of the correct chemical composition is obtained. Generally speaking water and CO_2 are oxidising and decarburising to steel at high temperatures. Hydrocarbons and carbon are carburising and, depending on the temperature, a CO_2/CO balance can be achieved which is neutral to carbon steel.

It is clear, therefore, that if avoidance of oxidation of the iron and some carburisation is required, then atomisation with nitrogen, either pure or impure, with an excess of injected hydrocarbon compared with the injected water is appropriate. In the more usual case it is required to avoid oxidation of the iron and at the same time to approach neutral conditions either with slight carburisation or with slight decarburisation. In such a case the ratio of injected hydrocarbon to injected water is carefully matched. The exact amounts of hydrocarbon and water depends partly on the presence or otherwise of oxidised gases in the nitrogen and on the chemical composition of the hydrocarbon. When the N_2 is fairly pure and the hydrocarbon is a light fraction-long chain saturated compound the proportion of liquid hydrocarbon to water is approximately 1:1 by weight. More hydrocarbon will give carburising effects and less hydrocarbon will give decarburising and eventually oxidising conditions.

The injection of liquid hydrocarbons and water may be accomplished in two main ways. The first way is to mix a fine spray of the liquids with the nitrogen stream near to, but before it enters the main atomisation chamber. This will be called the carburettor procedure. The other method is to inject the liquids through nozzles positioned in the main atomisation chamber. This will be called the direct injection procedure. The object of both procedures is to mix the fluids as completely as possible and at the same time to make the atomisation as efficient as possible.

There are several possible variations involving the same principle and concept such as:

(a) The injection of hydrocarbon and water into the gas stream by means of separate nozzles using either the carburettor or the direct injection procedure;

(b) The injection of hydrocarbon and water into the gas stream by means of concentric nozzles using either the carburettor or the direct injection procedure;

(c) The injection of water by the carburettor procedure and hydrocarbon by the direct injection procedure;

(d) The injection of hydrocarbon by the carburettor procedure and water by the direct injection procedure.

From amongst the possible variations it

has been found that the most satisfactory results are obtained by the variation (b). This is the preferred variation which will be described here although it will be understood that the other variations (a), (c) and (d) produce acceptable results.

For the purpose of explaining the invention further, the atomising of low carbon steel will be taken as an example, although it is not intended to imply that the invention is any less applicable to other metals. The operation of the invention can best be seen by reference to Fig. 1 which shows a vertical section through an equipment for atomising low carbon steel by means of impure nitrogen with liquid hydrocarbon and water injected from concentric nozzles using the carburettor procedure. Fig. 2 shows in greater detail a section through the concentric carburettor arrangement shown in Fig. 1. Fig. 3 shows a section through the atomising nozzles when the direct injection procedure is used.

Molten steel is poured into the refractory lined tundish (1) from where it runs through a refractory nozzle (2) to fall in a liquid stream (3) into the atomising chamber (4). Nitrogen is supplied at a pressure of 150 psi to an axi-symmetric array of nozzles (5) which are directed towards the falling stream of liquid steel (3) at an angle of approximately 15° to the vertical. The pipe (6) supplies the nitrogen to the nozzles (5). A light hydrocarbon such as paraffin or kerosene, and water are metered under high pressure in excess of the pressure of nitrogen, to the concentric nozzle (7) which protrudes into the nitrogen gas stream. The liquid hydrocarbon and water issuing from the concentric nozzle (7) are converted into a fine spray and the droplets of the liquids are carried along the pipe (6) to the main atomising nozzles (5) which exhaust into the atomising chamber (4) which operates at pressures slightly above atmospheric.

The concentric nozzle arrangement from Fig. 1 is shown in greater detail in Fig. 2 where, for example, the water is fed through the central pipe (8) and the hydrocarbon is fed through the outer pipe (9) of the concentric nozzle. The concentric nozzle is positioned at the narrowest part of a venturi (10) so that liquid film formation on the walls of the pipe (6) in the vicinity of the venturi is minimised by the high gas flow at that point. It is necessary that the pumps supplying the hydrocarbon and water have a positive displacement such that metered volumes of the liquids are delivered irrespective of the nitrogen pressure in the pipe (6).

The jets of nitrogen, hydrocarbon and water issuing from the nozzles (5) shown in Fig. 1 impinge on the stream of liquid steel (3) breaking it into small droplets which

are rapidly chilled and form a shower of solid powder particles (11). The solid powder particles collect at the bottom of the atomisation chamber (4) and are discharged by the Archimedian screw (12) into a receiving chamber (13). The discharge mechanism is sealed into the atomisation chamber (4) so that gas leakage is minimised. The used gas which is of high calorific value flows out of the ports (14).

The invention described above enables dry steel powder to be produced with a much smaller usage of nitrogen of lower purity than is normally used in gas atomising. It also increases the rate of chilling of the liquid metal droplets formed by atomisation. The way in which the invention operates is as follows. The liquid hydrocarbon and water injected under pressure into the nitrogen stream are formed into a fine spray by the concentric nozzle (7) and the droplets are carried along in the nitrogen stream. Some of the hydrocarbon and water evaporate causing the temperature of the mixed gases to be lowered because of the latent heat of vaporisation absorbed. The remainder persists as liquid droplets until the jet of nitrogen carrying the droplets meets the descending stream of liquid steel. The high pressure nitrogen disintegrates the metal stream and the liquid droplets are immediately evaporated so absorbing a great deal of heat from the molten steel. On changing into hydrocarbon vapour and steam a great expansion of volume occurs which reinforces the disintegrating effect of the nitrogen and promotes further atomisation. In addition, the hydrocarbon vapour is decomposed by the high temperatures involved to form hydrogen, carbon and lighter residual hydrocarbons. This decomposition is accomplished by a further increase in gas volume which aids atomisation, and by a further chilling of the liquid steel brought about by the endothermic decomposition. The presence of steam at high temperatures in contact with free carbon and iron causes the formation of CO and H₂ by the water-gas reaction described previously. The reaction is endothermic leading to further heat absorption from the molten steel and is accompanied by a further gas volume increase. To summarise, the increase in gas volume caused by vaporisation and reaction effectively increases atomisation. The evaporation of the liquid droplets and the endothermic reactions absorb large quantities of heat causing a marked chilling of the atomised steel. The prevailing reducing conditions prevent the oxidation of the steel during atomisation and the gas offtake from the process is a valuable fuel of high calorific value.

A similar situation develops when water and hydrocarbon are injected directly into the atomisation chamber. In this case the

carburettor arrangement is abolished and the pipe (6) conveying nitrogen terminates at the atomiser where the hydrocarbon and water are injected directly. The preferred arrangement is shown in Fig. 3 which shows a section through an atomiser fitted with a ring of six concentric nozzles (15) disposed axi-symmetrically at an angle of 15° to the stream of molten steel (16). Nitrogen at, for example, a pressure of 150 psi is supplied from the manifold (17) through the outer part of the nozzle (15). A concentric nozzle similar to that described in Fig. 2 allows a metered high pressure jet of water and hydrocarbon to issue into the nitrogen stream. In this case for example the water is metered and pumped through the central pipe (18) and the hydrocarbon is metered and pumped through the outer pipe (19) of the concentric nozzle at high pressure. The hydrocarbon and water are formed into a fine spray in the nitrogen stream immediately on issuing from the main nozzle (15) and before reaching the molten metal stream. The jets of mixed nitrogen, hydrocarbon and water impinge on the molten metal stream causing it to be atomised into fine liquid particles (20) which solidify in flight to form powder. The reactions that proceed when the jets of mixed nitrogen, hydrocarbon and water impinge on the molten metal stream are exactly as described before.

The benefits and disadvantages of the two procedures are as follows. The carburettor procedure gives good mixing of the liquid droplets with the nitrogen stream and the equipment is simple to construct because only one large concentric nozzle is needed. A disadvantage is that liquid films may form on the walls of the pipe and the atomiser manifold causing erratic operation. The direct injection procedure avoids all problems of liquid film formation at the cost of greater equipment complexity. It also has the advantage of injecting the liquid at high pressure in the direction of the atomising jets thus promoting better atomisation. While both procedures give very satisfactory results the direct injection procedure is most favoured.

In order to gauge the benefit that can be obtained by the use of the invention, the following example can be given. The gas atomising of liquid steel on a large scale by nitrogen in the usual way would require between 4 and 6 cu.ft. of nitrogen per lb. of steel in order to obtain sufficient solidification before collection of the powder. Utilising the invention, it is possible, for example, by using 2 cu.ft. of nitrogen of lower purity per lb. of steel and injecting 0.05 lbs. of a sulphur-free paraffin oil together with 0.03 lbs. of water per lb. of steel, to obtain better atomisation, a finer powder free from oxide, and rapid solidification.

It is important to reduce as far as possible the separation of unreacted carbon which may result from the cracking of the hydrocarbon at high temperatures. Good mixing of the hydrocarbon with the water and the nitrogen, and the direction of the jets onto the stream of molten steel are beneficial in this respect. So too is the use of concentric nozzles for delivery of the hydrocarbon and the water rather than the use of separate nozzles. The lighter hydrocarbon fractions show less tendency to the formation of free carbon than the heavier fractions and are preferred.

In both cases, the exit gas is a high calorific fuel at high temperatures. After extracting any fine iron dust by electromagnetic separators, the exit gas may then be used as a very valuable high temperature gaseous fuel for furnaces. In a steel plant it could also be injected into the blast furnace, thereby using both the gaseous fuel and the surplus iron dust. The calorific value of the fuel is enhanced by the endothermic reactions proceeding in the spraying chamber. In other words, some of the unwanted heat in the liquid steel when atomised is stored chemically in the waste gases from which it can be liberated and used by subsequent combustion. Thus a most useful transfer of energy takes place from a situation where heat needs to be extracted, i.e. chilling after atomisation, to a situation where heat energy is required, i.e. the burning of the exit gases.

The invention is particularly beneficial where it is required to manufacture dry metal powder from molten metals. Fine chilled powders may be obtained by this means. The formation of coarsely atomised solidified metal particles is also greatly facilitated because the chilling effect of injected hydrocarbons and water is sufficient to freeze at least the outside skins of such particles to a considerable depth before they are collected. By conventional gas atomising procedures, the chilling and freezing of particles, say, 1 mm diameter, before collection is difficult because of their relatively small surface/volume ratio. The invention enables the manufacture of such coarsely atomised particles to be conducted without difficulty.

It is to be noted that by using an impure nitrogen in the form of a flue gas the atomisation process is conducted using only air, water and hydrocarbons as basic fluids for atomising. Moreover, the full heat energy of the hydrocarbons can be utilised for such purposes as steam raising irrespective of the fact that it is also being used as an integral part of the atomising process.

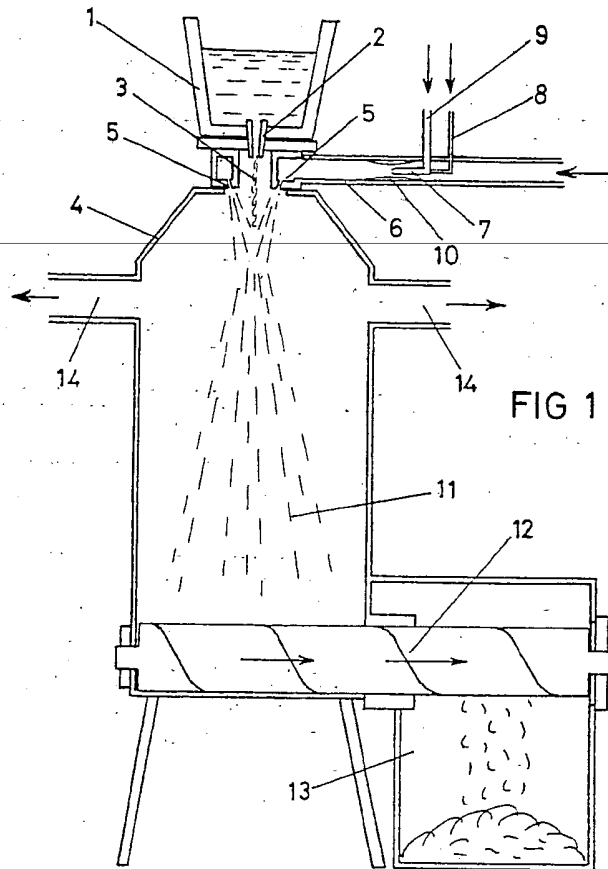
WHAT I CLAIM IS:—

1. A method for making metal and alloy powders or particles by atomising a stream

- of molten metal with a mixture of fluids comprising nitrogen, which may be relatively impure, hydrocarbons and water, the mixture comprising more than 10% nitrogen, the fluids causing the molten metal to be disrupted to form liquid particles which subsequently solidify.
2. A method according to claim 1 in which liquid hydrocarbons and water are introduced into the nitrogen stream in the form of fine sprays, the pressurised mixed fluids issuing from an atomising nozzle or nozzles as a jet or jets which impinge on the molten metal stream to cause atomisation.
3. A method according to claims 1 or 2 in which the nitrogen may contain water vapour, carbon monoxide, carbon dioxide, hydrogen and oxygen as impurities.
4. A method according to claim 1 in which all or part of the hydrocarbon is a gas.
5. A method according to any of claims 1 to 4 in which the mixed atomising fluids are formed by entraining sprays of hydrocarbons and water in the nitrogen stream in the manner of a carburettor before the mixed fluids enter the molten metal atomiser.
6. A method according to any of claims 1 to 4 in which the mixed atomising fluids are formed by entraining sprays of hydrocarbons and water in the nitrogen stream in the molten metal atomiser.
7. A method according to any of claims 1 to 4 in which the mixed atomising fluids are formed by discharging nitrogen, hydrocarbons and water in the atomising chamber by means of independent nozzles arranged so that the various jets and sprays are mixed in the atomising chamber.
8. A method according to any of claims 1 to 4 in which the mixed atomising fluids are formed by sprays of hydrocarbons and water in different positions from one another, which positions may be in a carburettor device, in the molten metal atomiser or independently in the atomising chamber.
9. A method according to any of claims 1 to 8 in which the metal stream to be atomised by the mixed fluids is formed into a curtain or an annular shape.
10. A method according to any of the previous claims in which the quantities of hydrocarbon and water are carefully controlled, taking into account the purity and known composition of the nitrogen, to obtain the required reducing, neutral or oxidising conditions in the atomising chamber when molten metals are being atomised.
11. A method according to any of the previous claims in which the quantities of hydrocarbon and water are carefully controlled, taking into account the purity and known composition of the nitrogen, to obtain the required carburising, neutral or decarburising conditions in the atomising chamber when molten iron or steel is being atomised.
12. Apparatus for atomising metals and alloys comprising a chamber, means for atomising a molten metal stream with a combined stream of nitrogen, hydrocarbon and water, means for collecting and removing the powder after solidification and means for removing the gas mixture after use.
13. Apparatus according to claim 12 in which liquid hydrocarbons and water are introduced into the nitrogen stream in the form of fine sprays, the pressurised mixed fluids being forced through nozzles to impinge on the stream of molten metal to cause atomisation.
14. Apparatus according to claims 12 or 13 in which the mixed atomising fluids are formed by entraining sprays of hydrocarbons and water in the nitrogen stream in the manner of a carburettor before the mixed fluids enter the molten metal atomiser.
15. Apparatus according to any of claims 12 to 14 in which the mixed atomising fluids are formed by entraining sprays of hydrocarbons and water in the nitrogen stream in the molten metal atomiser.
16. Apparatus according to any of claims 12 to 15 in which the mixed atomising fluids are formed by discharging nitrogen, hydrocarbons and water in the atomising chamber by means of independent nozzles arranged so that the various jets and sprays are mixed in the atomising chamber.
17. Apparatus according to any of claims 12 to 16 in which the mixed atomising fluids are formed by sprays of hydrocarbons and water in different positions from one another, which positions may be in a carburettor device, in the molten metal atomiser or independently in the atomising chamber.
18. A method of making metal powders or particles according to any of claims 1, 2, 10 or 11 substantially as herein described.
19. Metal powders or particles when produced by the method claimed in any of claims 1, 2, 10 or 11.
20. An apparatus according to any of claims 12 to 17 substantially as herein described with reference to Figures 1, 2 and 3 of the accompanying drawings.

A. R. E. SINGER.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1975.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.



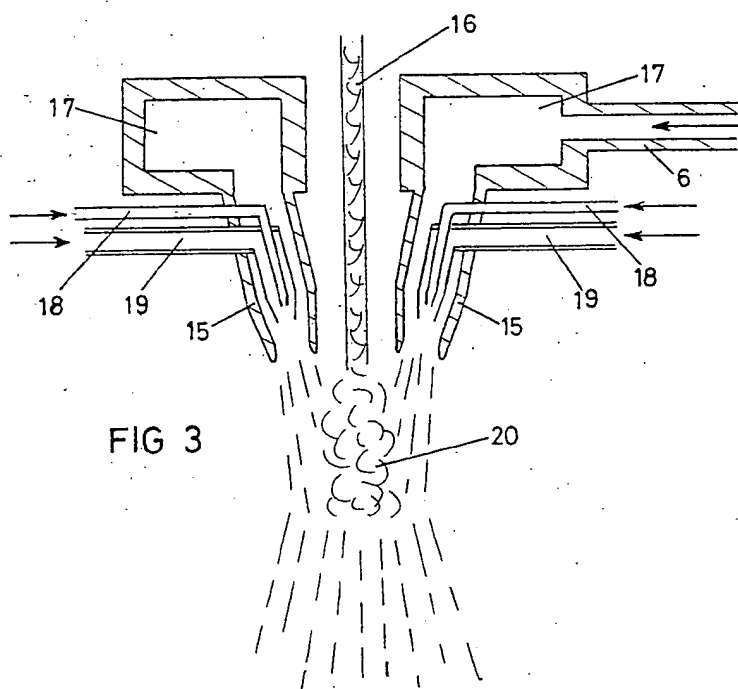
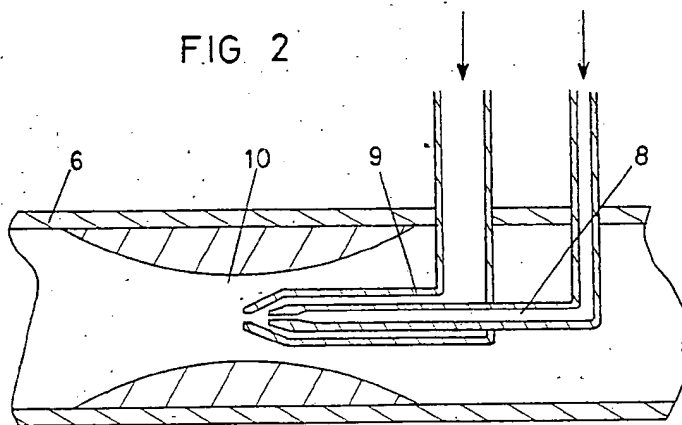
1413651

COMPLETE SPECIFICATION

2 SHEETS

This drawing is a reproduction of
the Original on a reduced scale
Sheet 2

FIG 2



THIS PAGE BLANK (USPTO)